

REMARKS/ARGUMENTS

Reconsideration and allowance of the instant application are respectfully requested. Claims 6, 8, 10, and 19 remain in this application. Claims 1-5, 7, 9, 11-18, and 20 are canceled. Enclosed is a (non-machine) translation of Ueda.

Claims 1-2, 4-6, 8-12, and 14-16 stand rejected under 35 USC 103(A) as unpatentable over Ueda (JP 200303132) in view of Shinji (JP 08-120389 English Machine Translation). Claims 1-2, 4, 5, 9, 11, 12, and 14-16 have been canceled. Claims 18-20 stand rejected under 35 USC 103(a) as unpatentable over Ueda in view of Shinji and Baba et al. (JP 58-040495). Claims 18 and 20 are canceled. In regard to claims 6, 8, 10, and 19 these rejections are respectfully traversed.

Claims 6, 8, and 10 are directed to a brazed part. The brazed part is made in accordance with fluxless brazing under a controlled atmosphere of nitrogen and using an aluminum alloy strip or sheet containing 0.01 to 0.5% of yttrium and the elements as claimed, and coated on at least one face with a brazing aluminum alloy as claimed. Thus arguments in the Office Action regarding “suitable for” fluxless brazing under controlled atmosphere of nitrogen are not relevant to these claims since the pending claims positively recited a brazed part made with fluxless brazing under nitrogen. None of the prior art teaches such a brazed part. Nor is there any reason one skilled in the art would have modified a piece prepared under vacuum to provide a piece prepared under a nitrogen atmosphere.

In the field of brazing, common prior art processes include:

Nocolok brazing which occurs with flux under controlled atmosphere and is one of the most commonly used processes along with vacuum brazing. Such brazing is possibly used by Baba.

Fluxless brazing under vacuum is brazing taught and used by Ueda, Shinji, and possibly by Baba.

The present invention is directed to a brazed part prepared by fluxless brazing under a controlled atmosphere of nitrogen which is a different process from both the Nocolok process and brazing under vacuum.

The Office Action considers on page 6, line 8, that the core and brazing alloy in Ueda are the same as claimed. This position is respectfully disagreed with. Ueda does not teach or suggest how to select a core composition useful for fluxless brazing under nitrogen. Ueda

selects the core composition in view of a **different brazing process under vacuum**. Further the brazing alloy in Ueda does not contain “at least one element for modifying the surface tension of the alloy, the element selected from the group consisting of Ag, Be, Bi, Ce, La, Pb, Pd, Sb, and mischmetal” as claimed. Ueda only teaches Si + Ge and possibly Mg.

A precise translation of Ueda is attached, wherein, on page (3), second column, in the middle part can be found: “other elements may be added as well within the ranges of ***not inhibiting the effects*** of the present invention” (emphasis added.) Since the elements of the instant claims are for modifying the surface tension, clearly one skilled in the art would not have considered such elements suitable for Ueda as such elements would have modified the Ueda composition. That is, the **dissuading teaching** in Ueda would lead one skilled in the art away from the addition of other elements as claimed. Ueda does not teach the addition of Ag, Be, Bi, Ce, La, Pb, Pd, Sb, or Mischmetal or any effects thereof and one skilled in the art would have considered **only Si, Ge and Mg** to avoid any risk.

Furthermore, one skilled in the art when considering Ueda, would be directed away from the use of Y in its alloy because such element, although mentioned, does not provide ideal results in Ueda. That is, one skilled in the art may choose for the core, an alloy prepared from several elements: Mn, Ca, Li, Sr, Sc, Y, Ti, Zr, V, Nb, Co, Ni, and Ta but Ueda actually teaches away from the use of the claimed core for several reasons:

1) Ueda is directed to a vacuum brazing process and not a brazing without flux under nitrogen as claimed and there is no teaching or suggestion that a brazing process under vacuum is equivalent to a brazing process under a nitrogen atmosphere.

2) The additive elements are used in Ueda to improve the resistance to erosion (“erosion inhibiting elements” on page 3, second column, beginning of paragraph [0011]). This problem has nothing to do with avoiding the use of a flux when brazing under a nitrogen atmosphere.

3) The element Y, mandatory in the core alloy as claimed, is not at all, even for anti-erosion reasons, considered as the best one or the one to choose by Ueda. In reality, Ueda is clearly teaching (see end of paragraph [0011]) that Ca and Li are particularly preferable, and this is confirmed by the results of infiltration depth tests on page (6) where only Ca (line 4) and Li (line 8) containing materials appear with no infiltration, whereas the infiltration depth is from 20 to 75 for Y, so at the same level or even worse than for Zr, Ti, Co or Ta. Hence Y is not ideal for in a core for brazing under vacuum and there is no reason to expect that it

would provide good results for a brazed part prepared under a nitrogen atmosphere.

4) The best way taught by Ueda (see claims 3 and 4, as well as page 5, paragraph [0020]), is not to place the erosion inhibiting element in the core but between the core and the clad in a specific “corrosion inhibiting layer.”

Thus, one skilled in the art has no reason to choose for the core an alloy containing Y when considering Ueda, that deals with another brazing process, wants to solve a completely different problem (erosion), for which Y is not the best choice, and in which the best way taught is to place the erosion inhibiting element in an intermediary “corrosion inhibiting layer.”

Even assuming Y is used in the core, one skilled in the art would have been taught away from the claimed invention, by the fact that adding in the clad addition elements other than Si, Ge and/or Mg means risk of inhibiting the effect of Ueda's invention which Ueda specifically teaches against. (Again it is noted that these elements are added in the claimed invention to modify the surface tension.)

Even if the one skilled in the art retains by chance such an alloy as in Ueda and with Y as the additive element, one has absolutely no reason to retain the Shinji teaching to modify Ueda and even less to choose an alloy containing Bi as in the claimed invention in order to allow for a fluxless brazing under a nitrogen atmosphere for again several reasons:

1) Shinji is directed to improving the intergranular corrosion facing “working fluids” circulating in the heat exchanger (see page 1/10, [0002], page 2, [0004]: “making clad material work as a sacrificial anode”) which is a completely different problem as the one solved by the claimed invention.

2) Shinji is not directed to brazing under a controlled atmosphere and especially a nitrogen atmosphere. Similar to Ueda, the process used for the examples (see page 8/10) is vacuum brazing. One skilled in the art would thus not turn to this reference to solve issues with brazing under a nitrogen atmosphere.

3) Shinji deals with Al-Cu alloys with Cu greater than 1.5 % for the core, which, contrary to the position in the Office Action, is not at all the same as in the claimed invention (where $\text{Cu} < 1.0\%$). **Shinji precisely teaches that the interaction between clad and core is crucial** (see [0007]: “adding a little Bi into an Al-Cu system alloy” and [0018] “the CuAl_2 deposits easily with the priority portion/of a grain boundary to the part of Bi,”) so one skilled in the art would not have turned to Shinji to obtain the core of the instant claims.

4) When the clad alloy cited in "Shinji" (AlSiMgBi) does include Bi, it is associated with Mg, in the same way as above, to improve vacuum brazing only. Once again, brazing under vacuum requires different considerations than brazing under a nitrogen atmosphere and produces different brazed parts.

There is simply no teaching or suggestion in Shinji of using an element selected from the group consisting of Ag, Be, Bi, Ce, La, Pb, Pd, Sb, and mischmetal in a brazing alloy for use with the aluminum core as claimed, in order to allow fluxless brazing under nitrogen atmosphere.

Finally similar to Shinji, Baba is directed to improving the corrosion behavior by creating a sacrificial anodic effect for a fin material by adding Sn. The fin material contains a core composed of an Al-Sn-Mn-Cu alloy with addition of 0.2-1.5 Zn, which is, as for the core alloy of Shinji, fully different and not transposable to the instant claims.

Baba does not utilize the addition of Bi (moreover associated to Zn, Sn and Mn) to promote the suppression of a flux when brazing under nitrogen, but in order to create an anodic sacrificial effect. The purpose of Baba is thus very different than that of the instant claims. As a consequence, in contrast to the conclusion in the Office Action, there is no teaching to add the Bi element as taught by Baba in order to promote the suppression of a flux when brazing under nitrogen. There is no teaching in "Baba" to add the Bi element in order to enable the suppression of a flux when brazing under nitrogen.

Hence, Ueda in view of Shinji and Ueda in view of Shinji and Baba do not teach or suggest the instant claims.

Request for Interview

If the rejections are maintained, the courtesy of an interview is respectfully requested by contacting the undersigned.

CONCLUSION

If any further fees are required or if an overpayment is made, the Commissioner is authorized to debit or credit our Deposit Account No. 19-0733, accordingly.

All rejections having been addressed, applicants respectfully submit that the instant application is in condition for allowance, and respectfully solicit prompt notification of the same.

Respectfully submitted,

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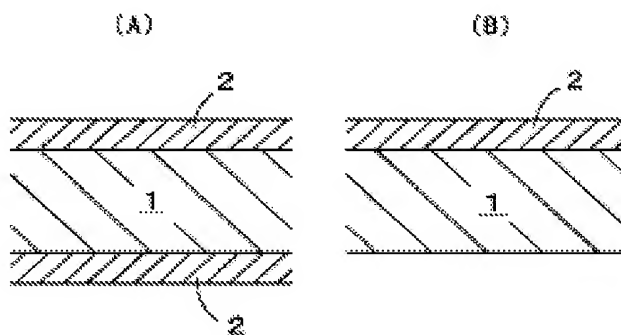
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(54) [Title of the Invention] Aluminum Alloy Brazing Sheet Excellent at Erosion Resistant Characteristics

(57) [Abstract]

[Problems to Be Solved] To provide an Al alloy brazing sheet excellent at erosion resistant characteristics.

[Solution] On both sides or one side of a core material 1 composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter) is laminated a brazing filler metal 2 composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge to form an Al alloy brazing sheet. The core material 1 is composed of an Al alloy containing, in addition to Mn, 0.1 – 5.0% Ca, 0.1 – 10.0% Li, 0.05 – 0.8% Sr, 0.05 – 0.8% Sc, 0.05 – 1.0% Y and a prescribed amount of one kind selected from Ti, Zr, V, Nb, Co, Ni, Ba, Be and Ta. The abovementioned Ca and the like can control or prevent erosion by depositing and fixing Si and Ge, which infiltrate into the core material from the brazing filler material, as compounds.



[We claim]

[Claim 1] An AL alloy brazing sheet excellent at erosion resistant characteristics, the AL alloy brazing sheet being formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge, wherein the core material is composed of an Al alloy containing, in addition to Mn, one kind selected from 0.1 – 5.0% Ca, 0.1 – 10.0% Li, 0.05 – 0.8% Sr, 0.05 – 0.8% Sc, 0.05 – 1.0% Y, 0.17 – 1.0% Ti, 0.3 – 1.0% Zr, 0.2 – 1.0% V, 0.05 – 1.0% Nb, 0.1 – 0.5% Co, 0.05 – 0.5% Ni, 0.05 –

0.8% Ba, 0.05 – 0.8% Be and 0.05 – 1.0% Ta.

[Claim 2] An AL alloy brazing sheet excellent at erosion resistant characteristics, the AL alloy brazing sheet being formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge, wherein the core material contains, in addition to Mn, at least one kind selected from Ca, Li, Sr, Sc, Y, Ti, Zr, V, Nb, Co, Ni, Ba, Be and Ta and wherein the contents of contained elements satisfy the following expression (1) and expression (2):

$$\begin{aligned} & \frac{[Ca]}{0.1} + \frac{[Li]}{0.1} + \frac{[Sr]}{0.05} + \frac{[Sc]}{0.05} + \frac{[Y]}{0.05} + \frac{[Ti]}{0.17} + \\ & \frac{[Zr]}{0.3} + \frac{[V]}{0.2} + \frac{[Nb]}{0.05} + \frac{[Co]}{0.1} + \frac{[Ni]}{0.05} + \frac{[Ba]}{0.05} + \\ & \frac{[Be]}{0.05} + \frac{[Ta]}{0.05} \geq 1 \text{ ---- (1)} \\ & \frac{[Ca]}{5.0} + \frac{[Li]}{10.0} + \frac{[Sr]}{0.8} + \frac{[Sc]}{0.8} + \frac{[Y]}{1.0} + \frac{[Ti]}{1.0} + \\ & \frac{[Zr]}{1.0} + \frac{[V]}{1.0} + \frac{[Nb]}{1.0} + \frac{[Co]}{0.5} + \frac{[Ni]}{0.5} + \frac{[Ba]}{0.8} + \\ & \frac{[Be]}{0.8} + \frac{[Ta]}{1.0} \leq 1 \text{ ---- (2)} \end{aligned}$$

wherein [X] shows the content of an element X (weight %).

[Claim 3] An AL alloy brazing sheet excellent at erosion resistant characteristics, the AL alloy brazing sheet being formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge via an erosion inhibiting layer, the erosion inhibiting layer being composed of an Al alloy containing, in addition to Mn, one kind selected from 0.1 – 5.0% Ca, 0.1 – 10.0% Li, 0.05 – 0.8% Sr, 0.05 – 0.8% Sc, 0.05 – 1.0% Y, 0.17 – 1.0% Ti, 0.3 – 1.0% Zr, 0.2 – 1.0% V, 0.05 – 1.0% Nb, 0.1 – 0.5% Co, 0.05 –

0.5% Ni, 0.05 – 0.8% Ba, 0.05 – 0.8% Be and 0.05 – 1.0% Ta.

[Claim 4] An AL alloy brazing sheet excellent at erosion resistant characteristics, the AL alloy brazing sheet being formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge via an erosion inhibiting layer, the erosion inhibiting layer being composed of an Al alloy containing, in addition to Mn, at least one kind selected from Ca, Li, Sr, Sc, Y, Ti, Zr, V, Nb, Co, Ni, Ba, Be and Ta, wherein the contents of contained elements satisfy the following expression (1) and expression (2):

$$\begin{aligned} & \frac{[Ca]}{0.1} + \frac{[Li]}{0.1} + \frac{[Sr]}{0.05} + \frac{[Sc]}{0.05} + \frac{[Y]}{0.05} + \frac{[Ti]}{0.17} + \\ & \frac{[Zr]}{0.3} + \frac{[V]}{0.2} + \frac{[Nb]}{0.05} + \frac{[Co]}{0.1} + \frac{[Ni]}{0.05} + \frac{[Ba]}{0.05} + \\ & \frac{[Be]}{0.05} + \frac{[Ta]}{0.05} \geq 1 \text{ ---- (1)} \\ & \frac{[Ca]}{5.0} + \frac{[Li]}{10.0} + \frac{[Sr]}{0.8} + \frac{[Sc]}{0.8} + \frac{[Y]}{1.0} + \frac{[Ti]}{1.0} + \\ & \frac{[Zr]}{1.0} + \frac{[V]}{1.0} + \frac{[Nb]}{1.0} + \frac{[Co]}{0.5} + \frac{[Ni]}{0.5} + \frac{[Ba]}{0.8} + \\ & \frac{[Be]}{0.8} + \frac{[Ta]}{1.0} \leq 1 \text{ ---- (2)} \end{aligned}$$

wherein [X] shows the content of an element X (weight %).

[Detailed Explanation of the Invention]

[0001]

[Field of the Invention] The present invention relates to an AL alloy brazing sheet used as a material for parts of an automobile heat exchanger.

[0002]

[Prior Art] An automobile heat exchanger (e.g., an evaporator in a car air-conditioner) is constituted of a tube material and a fin material formed by processing an AL alloy brazing sheet, wherein both materials are brazed by vacuum brazing or the

like and then assembled. The abovementioned AL alloy brazing sheet is conventionally formed by cladding a brazing filler metal such as an Al-Si type alloy or an Al-Ge type alloy onto a core material composed of an Al alloy (e.g., JISA3003).

[0003] As part of efforts to reduce the weight of automobiles, there is recently a need for a reduction in the weight of heat exchangers and the thickness of AL alloy brazing sheets. When an AL alloy brazing sheet is made thinner, acceptable corrosion depth needs to be smaller as well. It has been known that corrosion is accelerated when erosion is significant because eutectic parts become priority corrosion pathways.

Accordingly, when an Al alloy brazing sheet is made thin, it is necessary to improve an Al alloy used in the core material of the brazing sheet not only in corrosion resistance but also in erosion resistance. As used herein, the term "erosion" refer to a phenomenon in which the brazing filler metal of an Al alloy brazing sheet infiltrates into the core material at the time of brazing and reduces the thickness thereof.

[0004] By way of example, a technology for controlling erosion is described in Published Unexamined Patent Application No. H2-153048, wherein a brazing sheet is cold-rolled (processing rate: 5 to 15%) in advance and then annealed at 145 to 195°C to prevent sub-grains from remaining so that recrystallization of a core material can be completed at the time of brazing.

[0005]

[Problems that the Invention is to Solve] However, the abovementioned technology adds cold processing and an annealing step, which are originally unnecessary, to production steps, thereby making the production steps complicated and the production cost increased.

[0006] The present invention was achieved in view of the abovementioned problems. The purpose of the present invention is to provide an Al alloy brazing sheet producible without adding any unnecessary production step.

[0007]

[Means of Solving the Problems] The present inventors paid attention to the fact that the erosion of a core material in an Al alloy brazing sheet was caused by the infiltration of Si or Ge contained in a brazing filler metal into the core material at the time of brazing and completed the invention based on the technological idea that erosion could be controlled or reduced by depositing these elements before they could infiltrate into the core material or on the surface part of the core material even when infiltration occurred.

[0008] In other words, the Al alloy brazing sheet according to Claim 1 of the present invention is formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge, wherein the core material is composed of an Al alloy containing, in addition to Mn, one kind selected from 0.1 – 5.0% Ca, 0.1 – 10.0% Li, 0.05 – 0.8% Sr, 0.05 – 0.8% Sc, 0.05 – 1.0% Y, 0.17 – 1.0% Ti, 0.3 – 1.0% Zr, 0.2 – 1.0% V, 0.05 – 1.0% Nb, 0.1 – 0.5% Co, 0.05 – 0.5% Ni, 0.05 – 0.8% Ba, 0.05 – 0.8% Be and 0.05 – 1.0% Ta.

[0009] As shown in Fig. 1, an Al alloy brazing sheet according to the present invention is basically formed by laminating, on both sides (See Fig. 1 (A)) or one side (See Fig. 1 (B)) of a core material 1 composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler

metal 2 composed of an Al alloy containing 0.8 (sic) – 13.5% Si or 0.4 – 5.5% Ge.

[0010] The reason why the core material 1 is formed of an Al alloy containing 0.05 – 2.0% Mn is that: Mn is effective in enhancing high-temperature strength and post-brazing strength; the effect is small if the content is less than 0.05%; and the strength enhancing effect saturates and processability declines if it exceeds 2.0%. The content of Mn is preferably in the range of 0.5 to 1.5%. In view of corrosion potential and the like, a core material may further contain 0.05 – 0.8% Cu, 0.05 – 0.5% Mg and 0.05 – 0.3% Ti. The reason why the brazing filler metal 2 is formed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge is that Si and Ge lower the liquidus temperature of Al so that fluidity is improved at the time of melting a brazing filler metal within these ranges. The purpose of the present invention can be achieved when an Al alloy brazing filler metal contains 6.0 – 13.5% Si or 0.4 – 5.5% Ge. Nevertheless, other elements may be added as well within the ranges of not inhibiting the effects of the present invention. As an example, the addition of 0.05 – 2.5% Mg is effective against oxide layers that inhibit brazing.

[0011] The invention described in Claim 1 is characterized in that an Al alloy constituting the core material 1 contains, in addition to Mn, one type selected from Ca, Li, Sr, Sc, Y, Ti, Zr, V, Nb, Co, Ni, Ba, Be and Ta (these elements may hereinafter be referred to as erosion inhibiting elements) within the abovementioned range (for each element, the preferable lower limit is the lower limit of the abovementioned prescribed range x 1.2, and the preferable upper limit is the upper limit of the abovementioned prescribed range x 0.8%). Those erosion inhibiting elements can effectively control erosion caused by the infiltration of Si or Ge into a core material from a brazing filler metal by binding to and fixing Si or Ge as Si compounds (silicides) or Ge compounds at the time of brazing. If the content of each erosion inhibiting element is less than its lower limit, Si or Ge infiltrating into a core material from a brazing filler metal cannot be sufficiently trapped as compounds, whereby the erosion inhibiting effect declines. On the other hand, if the content of each erosion inhibiting element exceeds its upper limit, a large number of intermetallic compounds containing coarse Al are formed, whereby mechanical characteristics and the like are adversely influenced. Among the abovementioned erosion inhibiting elements, Ca and Li are particularly preferable elements because these compounds tend to bind to Si and Ge.

[0012] The abovementioned content range of each erosion inhibiting element is when each element is added alone. Even if the amount of each element added is less than its lower limit, Si or Ge infiltrating from a brazing filler metal can be fixed as Si compounds or Ge compounds by compound addition, thereby controlling and preventing erosion.

[0013] The invention described in Claim 2 is an Al alloy brazing sheet further added with erosion inhibiting elements in an Al alloy constituting the core material, the Al alloy brazing sheet being formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a

$$\begin{aligned} & \{Ca\}/0.1 + \{Li\}/0.1 + \{Sr\}/0.05 + \{Sc\}/0.05 + \{Y\}/0.05 + \{Ti\}/0.17 + \\ & \{Zr\}/0.3 + \{V\}/0.2 + \{Nb\}/0.05 + \{Co\}/0.1 + \{Ni\}/0.05 + \{Ba\}/0.05 + \\ & \{Be\}/0.05 + \{Ta\}/0.05 \geq 1 \text{ ----- (1)} \\ & \{Ca\}/5.0 + \{Li\}/10.0 + \{Sr\}/0.8 + \{Sc\}/0.8 + \{Y\}/1.0 + \{Ti\}/1.0 + \\ & \{Zr\}/1.0 + \{V\}/1.0 + \{Nb\}/1.0 + \{Co\}/0.5 + \{Ni\}/0.5 + \{Ba\}/0.8 + \\ & \{Be\}/0.8 + \{Ta\}/1.0 \leq 1 \text{ ----- (2)} \end{aligned}$$

wherein [X] shows the content of an element X (weight %).

[0014] In the present invention, Expression (1) showing the lower limit of erosion inhibiting elements by compound addition specifies that the total contents/lower limit values of erosion inhibiting elements be equal to or greater than 1 (preferably equal to or greater than 1.2). Expression (2) showing the upper limit of erosion inhibiting elements by compound addition specifies that the total contents/lower limit values of erosion inhibiting elements be equal to or less than 1 (preferably equal to or less than 0.8). Thus, like Claim 1, Si or Ge infiltrating into a core material from a brazing filler metal can be fixed as Si compounds or Ge compounds using multiple erosion inhibiting elements by specifying the upper limit and the lower limit of the total values of added elements, thereby controlling and preventing erosion.

[0015] When the abovementioned erosion inhibiting elements are added more than 1.0% alone or in combination with two kinds or more thereof, a core material may be melted if a brazing temperature is high. Accordingly, the contents of added elements should be equal to or less than the concentration of an Al alloy on the solidus line + 1.0% at a brazing temperature at the time of high-temperature brazing.

[0016] In the invention described in Claim 1 and Claim 2, an Al alloy constituting a core material is added with erosion inhibiting elements alone or in combination with two kinds or more thereof, and Si or Ge infiltrating into a core material from a brazing filler metal is trapped as Si compounds or Ge compounds, thereby controlling and preventing erosion arising out of such an element. In this case, Si and Ge are trapped on the interface between the brazing filler metal and the core material or on the surface part of the core material; therefore it is not necessary for the entire core material to contain erosion inhibiting elements. The inventions according to Claim 3 and Claim 4 were made based on this fact.

[0017] The invention described in Claim 3 is an Al alloy

brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge, wherein the core material contains, in addition to Mn, at least one kind selected from Ca, Li, Sr, Sc, Y, Ti, Zr, V, Nb, Co, Ni, Ba, Be and Ta and wherein the contents of contained elements satisfy the following expression (1) and expression (2):

brazing sheet formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge via an erosion inhibiting layer, the erosion inhibiting layer being composed of an Al alloy containing one kind selected from the erosion inhibiting elements described in Claim 1, the erosion inhibiting elements each being within a prescribed range.

[0018] The invention described in Claim 4 is an Al alloy brazing sheet excellent at erosion resistant characteristics, the Al alloy brazing sheet being formed by laminating, on both sides or one side of a core material composed of an Al alloy containing 0.05 – 2.0% Mn (weight %, the same shall apply hereinafter), a brazing filler metal composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge via an erosion inhibiting layer, the erosion inhibiting layer being composed of an Al alloy containing at least one kind selected from the erosion inhibiting elements described in Claim 2, wherein the contents of contained elements satisfy the abovementioned expression (1) and expression (2).

[0019] As shown in Fig. 2, Al alloy brazing sheets of the inventions according to Claims 3 and 4 are each basically formed by laminating, on both sides (See Fig. 2 (A)) or one side (See Fig. 2 (B)) of a core material 1A composed of an Al alloy containing 0.05 – 2.0% Mn, a brazing filler metal 2 composed of an Al alloy containing 6.0 – 13.5% Si or 0.4 – 5.5% Ge via an erosion inhibiting layer 3. The reasons for limiting the contents of Mn contained in an Al alloy constituting the core material 1A, Si or Ge contained in an Al alloy constituting the brazing filler metal 2, and erosion inhibiting elements added to an Al alloy constituting the erosion inhibiting layer 3 are the same as those in the inventions according to Claims 1 and 2.

Components other than erosion inhibiting elements in the Al alloy constituting the erosion inhibiting layer 3 are not particularly restricted as far as the erosion inhibiting layer 3 can be laminated by cladding or the like between the brazing filler metal 2 and the core material 1A and is not melted at the time of brazing (i.e., its melting point is higher than a brazing temperature). The thickness of the erosion inhibiting layer is equal to or greater than 10 μ m, preferably equal to or greater than 50 μ m in order to achieve sufficient effects of the present invention. As brazing sheets tend to become thin, however, the thickness of the erosion inhibiting layer is equal to or less than 120 μ m, preferably equal to or less than 100 μ m.

[0020] The method for manufacturing an Al alloy brazing sheet according to the present invention is usually as follows: each raw material of a core material and a brazing filler metal or a core material, an erosion inhibiting layer and a brazing filler metal is melted and then processed to make a thin plate by hot rolling; those plates are laminated on each other and clad-rolled in the abovementioned order; after annealing, cold rolling is performed to process a product in progress to a prescribed thickness. Annealing may be properly conducted during or after the cold rolling as needed.

[0021] Published Unexamined Patent Application No. H9-310139 discloses a brazing sheet provided with an erosion inhibiting layer between an Al alloy core material and an Al alloy brazing filler metal. In this brazing sheet, however, pure aluminum is basically used in the erosion inhibiting layer. Pure aluminum tends to be recrystallized at the time of brazing, thereby preventing Si from infiltrating from a brazing filler metal. Therefore, the operation, effects and technological idea of the erosion inhibiting layer is different from those of the present invention.

[0022]

[Examples] We used a JISA3003A alloy composed of components as shown below as a base. We then added a variety of erosion inhibiting elements in such a manner as to attain the contents as shown in Table 1 and Table 2 below, melted each core material Al alloy, made a thin plate by hot rolling, and then performed cold rolling and annealing to make a core material thin plate. Afterward, we laminated brazing filler metal thin plates composed of an alloy of Al, 10% Si and 1.2% Mg on both sides of the abovementioned core material thin plate, clad-rolled, and then, after annealing, performed cold rolling and annealing to obtain a brazing sheet in which a brazing material (90 μ m x 2) was laminated on both sides of a core material having a thickness of 420 μ m as shown in Fig. 1

(A). At the time of annealing after cold rolling, we completely removed processing strain so that the brazing sheet could be completely annealed.

• Components in the JISA3003A alloy: 0.6% Si, 0.7% Fe, 1.2% Mn, 0.1% Zn (the remaining is substantially Al).

[0023] We added 3% or 7% strain (strain amount) to the abovementioned Al alloy brazing sheet by tensile processing, which was then thermally treated under imitated brazing conditions. Subsequently, we measured the infiltration depth of the core material caused by erosion under an optical microscope. The reason why we added the abovementioned strain to the Al alloy brazing sheet is that erosion was maximized in a conventional example (sample No. 1 in Table 1), wherein an 3003A1 alloy was used as a core material, when 3% to 7% strain was added (i.e., the most severe condition). At the time of the abovementioned thermal treatment, we heated the strain-added Al alloy brazing sheet in vacuum using an infrared image furnace, kept at 590°C for 2 minutes, and then cooled in the furnace. At the time of heating, the temperature increasing speed was 10°C/min between room temperature and 550°C, and 5°C/min between 550°C and 590°C. Although the cooling speed after retaining the temperature was not determined, we assumed that it was several tens °C/min.

[0024] We assessed erosion resistant characteristics by deciding whether the core material infiltration depth from the interface between the brazing filler metal before brazing and the core material is equal to or greater than 50 μ m or not in at least one of 3% and 7% strain-added materials. If the infiltration depth is equal to or greater than 50 μ m, no substantial improvement from the prior art can be expected. Production costs rather increases due to added alloy elements. If both of the 3% and 7% strain-added materials show less than 50 μ m, the thickness of a core material can be reduced such that industrial significance should be remarkable. Table 1 and Table 2 show the measured results of the core material infiltration depth, which is larger between the 3% and 7% strain-added materials. The core material infiltration depth, which is larger between the 3% and 7% strain-added materials, may be hereinafter referred to as the maximum core material infiltration depth.

[0025]

[Table 1]

| Sample No. | Erosion inhibiting elements | | Left-hand value of Expression (1) | Left-hand value of Expression (2) | Core material infiltration depth (μm) | Reference |
|------------|-----------------------------|-------------|-----------------------------------|-----------------------------------|--|----------------------|
| | Type | Content wt% | | | | |
| 1 | None | — | — | — | 80 | Conventional example |
| 2 | Ca | 0.04 | — | — | 70 | Comparative example |
| 3 | Ca | 0.22 | — | — | 40 | Invention example |
| 4 | Ca | 4.21 | — | — | 0 | " |
| 5 | Ca | 5.51 | — | — | — | Comparative example |
| 6 | Li | 0.04 | — | — | 50 | " |
| 7 | Li | 0.18 | — | — | 40 | Invention example |
| 8 | Li | 4.88 | — | — | 0 | " |
| 9 | Y | 0.04 | — | — | 70 | Comparative example |
| 10 | Y | 0.12 | — | — | 45 | Invention example |
| 11 | Y | 0.48 | — | — | 20 | " |
| 12 | Y | 1.22 | — | — | — | Comparative example |
| 13 | Ti | 0.11 | — | — | 50 | " |
| 14 | Ti | 0.19 | — | — | 20 | Invention example |
| 15 | Ti | 0.99 | — | — | 15 | " |
| 16 | Ti | 1.52 | — | — | — | Comparative example |
| 17 | Zr | 0.16 | — | — | 60 | " |
| 18 | Zr | 0.50 | — | — | 20 | Invention example |
| 19 | Zr | 1.51 | — | — | — | Comparative example |
| 20 | V | 0.03 | — | — | 50 | " |
| 21 | V | 0.48 | — | — | 30 | Invention example |
| 22 | V | 1.47 | — | — | — | Comparative example |
| 23 | Nb | 0.03 | — | — | 50 | " |
| 24 | Nb | 0.51 | — | — | 30 | Invention example |
| 25 | Nb | 1.22 | — | — | — | Comparative example |

[0026]

[Table 2]

| Sample No. | Erosion inhibiting elements | | Left-hand value of Expression (1) | Left-hand value of Expression (2) | Core material infiltration depth (μm) | Reference Type |
|------------|-----------------------------|--------------------|-----------------------------------|-----------------------------------|--|---------------------|
| | Type | Content wt% | | | | |
| 26 | Co | 0.04 | — | — | 50 | Comparative example |
| 27 | Co | 0.15 | — | — | 40 | Invention example |
| 28 | Co | 0.42 | — | — | 20 | " |
| 29 | Co | 0.55 | — | — | — | Comparative example |
| 30 | Ni | 0.04 | — | — | 50 | " |
| 31 | Ni | 0.06 | — | — | 40 | Invention example |
| 32 | Ni | 0.06 | — | — | 40 | " |
| 33 | Ni | 0.42 | — | — | 25 | " |
| 34 | Ni | 0.60 | — | — | — | Comparative example |
| 35 | Ta | 0.04 | — | — | 50 | " |
| 36 | Ta | 0.11 | — | — | 30 | Invention example |
| 37 | Ta | 0.02 | — | — | 10 | " |
| 38 | Ta | 1.18 | — | — | — | Comparative example |
| 39 | Li / Ca / Y | 0.08 / 0.08 / 0.03 | 2.20 | 0.05 | 40 | Invention example |
| 40 | Ti / Zr / Ta | 0.8 / 0.8 / 0.8 | 23.4 | 2.40 | — | Comparative example |

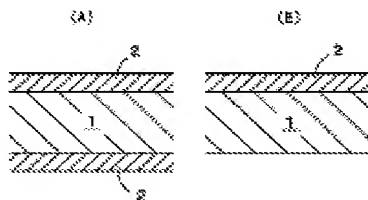
Note: The contents of the erosion inhibiting elements in No. 39 and No. 40 are described in the order of type.

[0027] The maximum core material infiltration depth was 80 μ m in sample No. 1, the conventional example where no erosion inhibiting element was added, while it was less than 50 μ m in all of the invention examples where erosion inhibiting elements were added within the ranges specified by the present invention, meaning excellent erosion resistant characteristics. In invention examples, non-recrystallized regions were observed in the core material after brazing; therefore the present invention is obviously different from the conventional erosion inhibiting technology that utilizes recrystallization.

[0028] In sample No. 5 where Ca was added more than the amount range specified by the present invention, a large amount of coarse deposits, which inhibit mechanical characteristics and the like, occurred in the core material, and therefore we did not measure the infiltration depth. Besides, we added about 5% Li in examples because Li is very expensive and so active a metal that explosion might occur. At any rate, an Al-Li binary system diagram shows that coarse Al-Li intermetallic compounds precipitate when the amount of Li exceeds 10.0%, whereby corrosion resistance and processability decline.

[0029] In sample Nos. 12, 16, 19, 22, 25, 29, 34 and 38 where Y, Ti, Zr, V, Nb, Co, Ni and Ta were added respectively more than the amount ranges specified by the present invention, coarse deposits, which were believed to deteriorate mechanical characteristics and corrosion resistance, occurred in the core material, and therefore we did not measure the infiltration depth. Besides, when multiple erosion inhibiting elements were added, the left-hand value of Expression (2) exceeded 1 (i.e., excessive addition) and coarse deposits occurred though the amount of each element added was equal to or less than the upper limit of single addition.

[Fig. 1]



[0030] Although we did not prepare a sample added with Ba or Be, it is obvious that these elements have erosion inhibiting effects similar to those of Ca and Sr because Ca and Sr, which have erosion inhibiting effects, are homologous elements in the periodic table and show chemically similar behavior. The reaction behavior of Ba and Be in an Al alloy is similar to that of Sr among the homologous elements; therefore we applied the upper and lower limits of Sr to these elements.

[0031]

[Effects of the Invention] In the present invention, a core material or an erosion inhibiting layer laminated next to a brazing filler material, which contains a prescribed amount of Si or Ge, is composed of an Al alloy containing prescribed erosion inhibiting elements alone or in combination with two kinds or more thereof. Accordingly, Si or Ge, which infiltrates into the core material from the brazing filler metal at the time of brazing, can be precipitated and fixed as Si compounds or Ge compounds, thereby controlling and preventing the infiltration of these elements into the core material. Thus, the present invention is excellent at erosion resistant characteristics.

[Brief Description of Drawings]

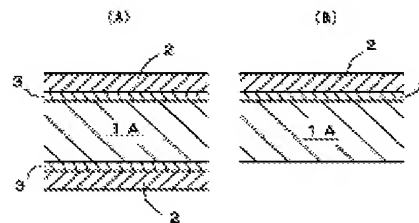
[Fig. 1] A schematic sectional view showing the structure of an Al alloy brazing sheet according to the present invention.

[Fig. 2] A schematic sectional view showing another structure of an Al alloy brazing sheet according to the present invention.

[Explanation of Reference Numerals]

- | | |
|-------|--------------------------|
| 1, 1A | core material |
| 2 | brazing filler metal |
| 3 | erosion inhibiting layer |

[Fig. 2]



(Continued from the front page)

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